Chain Dimensions and Concentration Fluctuations in Weakly and Strongly Interacting Polymer Blends

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Blending (or mixing) of macromolecules is widely used to tailor the properties of polymeric materials, and small-angle neutron scattering (SANS) has provided detailed information at the molecular level on the ability of different polymer species to mix or segregate at various thermodynamic conditions. For two decades, SANS data have been analyzed via the de Gennes "random phase approximation" (RPA), which is based on the assumption that the dimensions of polymer chains remain unchanged on mixing for all concentrations and temperatures. We investigated the effect of temperature and concentration on interrelation between dimensions of macromolecules and correlation length of the concentration fluctuations in blends using SANS and high concentration labeling methods and suggested a generic phase diagram, which specifies the range of validity of the RPA. Using scaling arguments, we demonstrate a parallel between the structure-property relationships in blends and solutions of polymers in small-molecule solvents and reveal the impact of the chain length of the polymeric solvent on the phase behavior of polymer blends. The results offer new insights into the universality of structure and thermodynamic properties in polymeric, liquid and supercritical solvents.